

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

Mo-6276/WW-5559

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/807251
To be Assigned

INTERNATIONAL APPLICATION NO.

PCT/EP99/07716

INTERNATIONAL FILING DATE

14 October 1999 (14.10.99)

PRIORITY DATE CLAIMED

16 October 1998 (16.10.98)

**TITLE OF INVENTION FLEXIBLE FILM PROVIDED WITH A FINE SPHERULITIC POLYAMIDE LAYER
CONTAINING NANOSCALAR, ANISOTROPIC NUCLEATING AGENTS**

APPLICANT(S) FOR DO/EO/US Holgers Eggers; Andreas Gasse; Bernd Eilers; Rudi Klein; Claudia Muller; Gregor Kaschel; Rainer Brandt; Dieter Neubauer

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

PTO FORM 1449 AND REFERENCES LISTED THEREIN; PRELIMINARY AMENDMENT W/ABSTRACT

U.S. APPLICATION NO. (if known, see 37 CFR 1.57)
To be Assigned **09/807251**INTERNATIONAL APPLICATION NO
PCT/EP99/07716ATTORNEY'S DOCKET NUMBER
Mo-6276/WW-555721. ☒ The following fees are submitted:

CALCULATIONS PTO USE ONLY

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):Neither international preliminary examination fee (37 CFR 1.482)
nor international search fee (37 CFR 1.445(a) (2)) paid to USPTO
and International Search Report not prepared by the EPO or JPO \$1000.00International preliminary examination fee (37 CFR 1.482) not paid to
USPTO but International Search Report prepared by the EPO or JPO \$860.00International preliminary examination fee (37 CFR 1.482) not paid to USPTO
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00International preliminary examination fee (37 CFR 1.482) paid to USPTO
but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00International preliminary examination fee (37 CFR 1.482) paid to USPTO
and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00**ENTER APPROPRIATE BASIC FEE AMOUNT =**

\$ 860.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$
Total claims	9 -20 =	0	x \$18.00	\$ 0.00
Independent claims	2 -3 =	0	x \$80.00	\$ 0.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00	\$ 0.00
TOTAL OF ABOVE CALCULATIONS =				\$ 860.00
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$ 0.00
SUBTOTAL =				\$ 860.00
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$
TOTAL NATIONAL FEE =				\$ 860.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$ 0.00
TOTAL FEES ENCLOSED =				\$ 860.00
				Amount to be refunded: \$
				charged: \$

\$

☐ A check in the amount of \$ _____ to cover the above fees is enclosed.☒ Please charge my Deposit Account No. 13-3848 in the amount of \$ 860.00 to cover the above fees.
A duplicate copy of this sheet is enclosed.c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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NAME42,552
REGISTRATION NUMBER

PATENT APPLICATION
Mo-6276
WW-5559

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF)
HOLGER EGGERS ET AL) PCT/EP99/07716
SERIAL NUMBER: TO BE ASSIGNED)
FILED: HEREWITH)
TITLE: FLEXIBLE FILM PROVIDED WITH)
A FINE SPHERULITIC POLYAMIDE)
LAYER CONTAINING)
NANOSCALAR, ANISOTROPIC)
NUCLEATING AGENTS)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

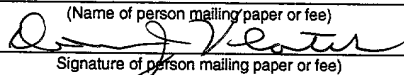
This preliminary amendment is being filed concurrently with the subject patent application. Upon granting a Serial Number and filing date, please amend the subject patent application as follows.

"Express Mail" mailing label number EK633383556US
Date of Deposit April 10, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch

(Name of person mailing paper or fee)


Signature of person mailing paper or fee)

Please amend the Application as follows.

IN THE SPECIFICATION:

Please replace the title at the top of page 1 with the following
--FLEXIBLE FILM PROVIDED WITH A FINE SPHERULITIC POLYAMIDE LAYER
CONTAINING NANOSCALAR, ANISOTROPIC NUCLEATING AGENTS--

IN THE ABSTRACT:

On a separate page, please add the following abstract.
-- FLEXIBLE FILM PROVIDED WITH A FINE SPHERULITIC POLYAMIDE LAYER
CONTAINING NANOSCALAR, ANISOTROPIC NUCLEATING AGENTS

ABSTRACT OF THE DISCLOSURE

Described is a film having at least one layer (I), which is composed of spherulitic crystallized polyamide containing solid, dispersed anisotropic nucleating fillers (A). The fillers (A) in layer (I) have an expansion of no greater than 10 nm in the numerical weighted average of all dispersed constituents of the fillers (A) in at least one direction (r_1), which can be freely selected for each dispersed constituent. The individual spherulites in layer (I) have a numerically averaged diameter of from 100 nm to 1000 nm in at least one plane which is perpendicular to the surface of the film. The numerically predominant portion of the dispersed fillers (A) in layer (I) form the crystal nucleus of a spherulite.--

A separate abstract page is included herewith.

IN THE CLAIMS:

Please replace Claim 2 with the following.
2. (Once Amended, Clean) The film of Claim 1 wherein said film contains one or more further polyamide-containing layers.

Please replace Claim 3 with the following.

3. (Once Amended, Clean) The film of Claim 1 wherein one or more layers (I) and/or one or more further polyamide-containing layers contain polyamide which is formed in a proportion amounting to at least 90 percent by weight from ϵ -caprolactam.

Please replace Claim 4 with the following.

4. (Once Amended, Clean) The film of Claim 1 wherein the individual spherulites are anisotropic in at least one layer (I).

Please replace Claim 5 with the following.

5. (Once Amended, Clean) The film of Claim 1 wherein the layer (I) forms the outer layer of the film.

Please replace Claim 6 with the following.

6. (Once Amended, Clean) The film of Claim 1 wherein said film contains one or more further polymeric layer(s) or contains between two layers a layer consisting of a metal or metal oxide or contains an imprint.

Please replace Claim 8 with the following.

8. (Once Amended, Clean) A method of using the film of Claim 1 for the production of containers on shaping/filling/sealing machines.

Please replace Claim 9 with the following.

9. (Once Amended, Clean) A method of using the film of Claim 1 for the packaging of foodstuffs.

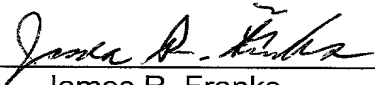
REMARKS

Claims in the case are 1 to 9. Claims 2-6, 8 and 9 have been amended herein.

Claims 2-6, 8 and 9 of the above-identified patent application have been amended as to form, for example, replacing "characterized in that" with --wherein--, and converting multi-dependent claims to dependent claims. Claims 8 and 9 have been changed from use claims to method claims by amendment herein. The title has been changed to correspond to the related International Patent Publication No. WO 00/23515. The patent application has also been amended to include an abstract on a separate page, which is included herewith. The amendments presented herein do not represent the entry of new matter into the application. Applicants respectfully request entry of this amendment.

Respectfully submitted,

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VERSIONS WITH MARKINGS TO SHOW CHANGES MADE

IN THE SPECIFICATION: (Marked-Up)

The following is a version of the title at the top of page 1, with markings to show changes made thereto in the present Preliminary Amendment.

[Flexible film with finely spherulitic polyamide layer containing nanoscalar, anisotropic nucleating agents]

FLEXIBLE FILM PROVIDED WITH A FINE SPHERULITIC POLYAMIDE LAYER
CONTAINING NANOSCALAR, ANISOTROPIC NUCLEATING AGENTS

IN THE CLAIMS: (Marked-Up)

The following are versions of the amended claims with markings to show changes made thereto in the present Preliminary Amendment.

2. (Once Amended, Marked-Up) The [F]film [according to] of [c]Claim 1[, characterised in that it] wherein said film contains one or more further polyamide-containing layers.

3. (Once Amended, Marked-Up) The [F]film [according to] of [c]Claim 1[, characterised in that] wherein one or more layers (I) and/or one or more further polyamide-containing layers contain polyamide which is formed in a proportion amounting to at least 90 percent by weight from ϵ -capro-lactam.

4. (Once Amended, Marked-Up) The [F]film of Claim 1 wherein [according to one of the previous claims, characterised in that] the individual spherulites are anisotropic in at least one layer (I).

5. (Once Amended, Marked-Up) The [F]film of Claim 1 wherein [according to one of the previous claims, characterised in that] the layer (I) forms the outer layer of the film.

6. (Once Amended, Marked-Up) The [F]film of Claim 1 wherein said film
[according to one of the previous claims, characterised in that it] contains one or
more further polymeric layer(s) or contains between two layers a layer consisting of
a metal or metal oxide or contains an imprint.

8. (Once Amended, Marked-Up) [Use of a film according to one of the
previous claims 1 to 6] A method of using the film of Claim 1 for the production of
containers on shaping/filling/sealing machines.

9. (Once Amended, Marked-Up) [Use of a film according to one of the
previous claims 1 to 6] A method of using the film of Claim 1 for the packaging of
foodstuffs.

-26-

FLEXIBLE FILM PROVIDED WITH A FINE SPHERULITIC
POLYAMIDE LAYER CONTAINING NANOSCALAR,
ANISOTROPIC NUCLEATING AGENTS

ABSTRACT OF THE DISCLOSURE

Described is a film having at least one layer (I), which is composed of spherulitic crystallized polyamide containing solid, dispersed anisotropic nucleating fillers (A). The fillers (A) in layer (I) have an expansion of no greater than 10 nm in the numerical weighted average of all dispersed constituents of the fillers (A) in at least one direction (r_1), which can be freely selected for each dispersed constituent. The individual spherulites in layer (I) have a numerically averaged diameter of from 100 nm to 1000 nm in at least one plane which is perpendicular to the surface of the film. The numerically predominant portion of the dispersed fillers (A) in layer (I) form the crystal nucleus of a spherulite.--

Flexible film with finely spherulitic polyamide layer containing nanoscalar, anisotropic nucleating agents

5 The present invention relates to a flexible polyamide-containing film with at least one layer consisting of polyamide, containing nanoscalar, anisotropic, nucleating fillers. The polyamide layer is distinguished by a finely crystalline spherulite structure. The film according to the invention exhibits, in addition to an outstanding optical appearance, a high degree of stiffness with good surface slip and low after-shrinkage. The invention also encompasses the use of the film for the manufacture
10 of packagings and also the use, in particular, for the packaging of foodstuffs, for imprinting as well as vapour deposition involving metallic layers or oxide layers.

Polyamide-containing films are used on a wide scale, inter alia in the packaging of foodstuffs.

15 Advantages of polyamide as a material are a high mechanical strength, a good barrier against oxygen, carbon dioxide and other non-polar gases as well as a high temperature resistance and scratch resistance.

20 A property of central importance that is demanded for the function of the film in packaging applications is an appealing appearance. A high gloss and also a low haze of the polyamide-containing film are demanded.

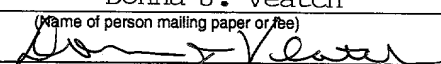
In addition, in many cases a high degree of stiffness with low elastic deformations is
25 necessary. This is a prerequisite, for example, for rapid and trouble-free running through packaging machines of conventional design. For example, high elastic deformations in the sealing station of packaging machines result in the formation of wrinkles in the wrapping. This is basically undesirable. The mode of operation of appropriate machines is familiar to the person skilled in the art and is described, for
30 example, in *The Wiley Encyclopedia of Packaging Technology* (edited by M. Bakker, D. Eckroth; John Wiley & Sons, 1986). The modulus of elasticity

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Donna J. Veatch

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according to DIN EN ISO 527 can be used as a suitable measure of the stiffness of a film.

5 Lastly, for many applications a good surface slip of the polyamide-containing film is demanded. In this connection a distinction has to be made between the surface slip of the film on a film surface of the same type and that on a metallic surface. A suitable measure of the surface slip is the coefficient of sliding friction according to DIN 53 375.

10 Polyamide is a partially crystalline thermoplastic polymer. In this connection the grain structure of the polyamide arising in a film is dependent to a great extent on the conditions of processing and also on the composition of the polyamide.

15 The slower the rate of cooling of the polyamide, the larger crystalline structures are able to evolve as a result of crystallisation. These structures interfere all the more with the optical appearance of the film, the larger they are. Coarsely crystalline PA films therefore exhibit an undesirably high haze and a likewise undesirably low gloss.

20 On the other hand, in the case of a rapid cooling from the melt, by virtue of the relatively slow crystallisation of polyamide in comparison with other thermoplastics such as polyethylene, for example, the greater part of the crystallisation process in the film is still not concluded with the shaping. Particularly in non-nucleated systems, on account of the cooling that is too rapid in relation to the rate of
25 crystallisation a metastable state can result which leads to a post-crystallisation of the polyamide over a longer time-interval directly following production. As a result of the diminution of the specific volume of the polyamide, which proceeds simultaneously with crystallisation, an after-shrinkage of such a film occurs on the roller. This is basically undesirable. Significant disadvantages arising from this are
30 a poor flatness of the film by reason of uneven shrinkage and also an increasing variation in the width of the film with increasing distance from the core of the roller. Furthermore, the film that has not crystallised out can only be controlled with

difficulty in the production process on account of its inadequate strength and high adhesive tendency.

5 Production of polyamide films can be effected in accordance with the flat-film process or the tubular-film process. Both the flat-film process and the tubular-film process offer the possibility of cooling the melt either very slowly or very rapidly. In the case of the tubular-film process, as a rule water is used as cooling medium for very rapid cooling operations.

10 Within the stated processes for the production of films, those processes are also possible in which the extruded melt is firstly cooled abruptly, in order then to be after-annealed in a further step at higher temperature. Advantages of such processes are the improved appearance of the PA films and also the slight after-shrinkage of the film on the roller by reason of the anticipation in the annealing. In addition to
15 this, with the post-crystallisation in the annealing step such films are given a higher strength and a better surface slip.

This process can also be realised both in the flat-film process and in the tubular-film process. Thus in the flat-film process an after-annealing may be effected on a roll
20 which is maintained at a higher temperature and situated downstream of the cold-set casting roll. In the tubular-film process an after-annealing may be effected either in a liquid, preferably water once again, or in air.

DE-A-33 08 296 discloses a process by which an initially abruptly chilled tube with
25 external polyamide layer can be subjected to after-annealing and moistening. The tube is therefore especially suitable for use as a sausage casing. The underlying process here consists in the chilling in a water bath and also in the subsequent annealing in a second water bath, as a result of which the tube is also moistened. Such systems have as an advantage a higher elastic extensibility than structures
30 produced conventionally. However, for the aforementioned reasons this is disadvantageous for the application as packaging films.

5 In addition to this, in many cases the flat-film process is preferred to the tubular-film process for economic reasons. Thus the output-rate of flat-film extrusion lines is regularly clearly higher and the manufacturing costs are correspondingly lower than in the case of comparable blown-film lines.

10 The state of the art is a flat-film process in which a flat film having the structure PP//PA6//PP or PE//PA//PE is firstly chilled via a cold casting roll, in order then to be post-crystallised on a downstream roll which is maintained at a high temperature. A characterisation by means of DSC of the PA layer of the films so obtained shows that the post-crystallisation of the PA which is otherwise conventional in the case of abrupt chilling can be avoided in this way. Accordingly, the films also exhibit no after-shrinkage on the reel. Other properties of the film composites produced in this way are not described.

15 However, such a process proves to be non-transferable to the conditions prevailing typically on the production scale: a rational and economical manufacture presupposes high web speeds and film widths in industrial practice.

20 As a rule, pure polyamide films and asymmetrical films having the structure PP//PA//PP or PE//PA//PE are also desirable. Although the obvious omission of the polyolefinic outer layers results in pure polyamide films, this entails considerable process-engineering problems which are presented in detail in the following examples. In principle, however, the polyamide films cannot be detached in plane manner from the cold-set casting roll at high web speeds. Thus flat films exhibit locally higher thicknesses in the marginal region than in the middle. This thickened edge is also designated in the following as a bead. In the region of the bead the film is, as a rule, also fixed to the casting roll by compressed air, so that the width of the film remains constant during the entire contact with the casting roll. By reason of 25 the low thermal conductivity of polyamide and other thermoplastics a slower cooling of the polyamide occurs in the region of the bead than in the middle of the film. As a result, a different grain structure forms in the bead than in the thinner region in the 30

middle of the film. In practice in the case of low casting-roll temperatures this leads to a shortening of the lengths of the film in the region of the bead. For this reason, and on account of the low strength of the amorphous polyamide film in the middle of the web, the film cannot be removed from the casting roll in plane manner but exhibits considerable wrinkles. The wrinkling leads, in turn, to a contact of the film with the subsequent roll, which is maintained at a high temperature, that is not uninterrupted over the entire surface area, so that upon conclusion of the post-crystallisation taking place there the deficient flatness of the film becomes irreversible. Further processing steps, such as lamination, imprinting or winding, for example, cannot be realised with such a film which does not lie flat.

WO 98/05716 discloses a process in which a tubular film or extruded sheet film is firstly cooled to temperatures from 0 to 30°C and subsequently in a second stage is heated to temperatures from 50 to 95°C. In this process such a film contains a polyamide that is filled with platelet-like fillers characterised by a ratio of diameter to length from 5:1 to 100:1, preferably phyllosilicates, in particular mica, in a proportion between 0.1 and 15 wt.%. The presence of the filler in this connection brings about, in particular, a lower permeability in relation to gases as well as an improved processing behaviour in the course of a subsequent biaxial stretching of the film. The fillers that are described, such as the aforementioned mica, exhibit diameters from 0.1 to 50 µm, preferably 1 to 20 µm. However, as can be discerned in connection with the examples according to the invention and the comparative examples, the use of such fillers does not generally prove to be advantageous in order to eliminate the disadvantages described above in connection with the flat-film process with a casting roll which is maintained at a low temperature and a downstream roll which is maintained at a high temperature. In addition, said fillers contribute to a fogging of the film to a considerable degree by virtue of their light-scattering action.

The addition of solid particles in the size range below one micrometer to polymeric matrices and, especially, polyamides has likewise been known for quite a long time. Such systems are described in concentrations between approximately 0.3 and 10

wt.%. Advantages arising in the case of higher proportions are increased stiffness values by reason of the reinforcing effect of the fillers as well as, in the case of platelet-like structure of the fillers that are used, also a superior oxygen barrier by reason of lengthened diffusion paths through the polymeric matrix. In particular, phyllosilicates are employed here that, in contrast to the phyllosilicate systems that are used in the aforementioned application WO 98/05716, can be integrated into the polyamide matrix by suitable treatment in a form decomposed in layers.

EP-A-358 415 discloses a film consisting of a polyamide resin with phyllosilicate uniformly dispersed therein, whereby the individual layers of the phyllosilicate may exhibit thicknesses around 1 nm and side-lengths up to 1 μ m. The layers are present in the polyamide matrix in separated form as a result of suitable decomposition. Films that are produced with this material in concentrations between 1.2 and 6.5 wt.% of phyllosilicate are distinguished, in comparison with those consisting of pure polyamide 6, by a distinctly enhanced oxygen barrier and stiffness. The slip properties are improved. The transparency of single-layer, amorphously chilled flat films as well as blown films with water cooling having the structure polyamide//coupling agent//PE-LD remains unchanged in comparison with pure polyamide 6. On the basis of cited examples of PA6 films with graduated content of phyllosilicate, the significant increase in the stiffness with simultaneous embrittlement in the range up to 3.0 wt.% of silicate becomes clear. Therefore such general structures are not suitable for the requirements at issue here.

WO 93/04118, as well as WO 93/11190 and WO 93/04117, each from the same applicant, disclose polymer nanocomposites with, likewise, platelet-like particles in the thickness range of a few nanometres, which are obtained not through incorporation by polymerisation but through mechanical incorporation. In particular, composites consisting of PA6 and montmorillonite or alternatively PA6 and silicates are described having a filler proportion between 0.27 and 9 wt.%. However, measurements on rods consisting of appropriate material in the case of a proportion amounting to 0.27 % silicate still show no increase in the bending strength. These materials can likewise be processed into films. Advantageous in

this case is a parallel alignment of the platelet-like particles in relation to the surface of the film. Applications as monofilm as well as the possibility of producing multilayer films are described. The films that are manufactured from this material may optionally be drawn, in order to obtain a still better orientation of the nanoparticles. The main advantage of such films in comparison with those without nanoscalar particles is a higher stiffness which, however, is always associated with a distinctly increased brittleness.

EP-A-818 508 discloses a mixture consisting of 60-98 % PA MXD6 with 2 to 40 % of an aliphatic polyamide, which once again contains inorganic particles in the nanometre size range. Mixtures are described, in particular, with PA 6 by way of aliphatic polyamide. In addition to these, multilayer films are described in the form of mouldings that can be produced therefrom. All the stated structures have as an advantage a high oxygen barrier which is also not impaired by sterilisation. Compared with a flat film consisting of pure PA6, a film according to the invention having the structure PA 6/(80 % PA MXD6 + 20 % PA 6 with nanoparticles)/PA 6 exhibits no appreciable improvement in transparency. The principal disadvantage of such structures having a high proportion of PA MXD6 is, once again, the increased brittleness of this material.

EP-A-810 259 likewise describes a polyamide moulding composition with nanodisperse fillers. By addition of sufficiently fine-particle oxides, hydrated oxides or carbonates, the barrier action of the polyamide that is desired in this patent can be improved. The particles preferably have a diameter of less than 100 nm and are employed in concentrations from 0.1 to 10 wt.%, preferably between 1 to 3 wt.%. Multilayer films are also described having at least one layer consisting of this moulding composition for the purpose of improving the oxygen barrier. However, the optical properties of a film consisting of polyamide 6 filled with a 1-wt.% silicate deteriorate significantly in comparison with the system without additives. Similarly, the elongation at tear deteriorates and the tensile modulus decreases. Corresponding films are therefore likewise generally unsuitable for the present application.

In view of the state of the art, the object was to make available a flexible polyamide-containing film that, with outstanding optical properties, exhibits a high degree of stiffness and good surface slip. Said film is intended to be capable of being produced in conventional lines for producing films, for economic reasons in particular in flat-film extrusion lines, reliably and at high speeds. Said film is furthermore intended to exhibit in the wound state only a minimal after-shrinkage that does not impair the quality of the reel.

In accordance with the invention, this was possible through provision of a film having at least one layer (I) consisting of substantially spherulitically crystallised polyamide containing solid, anisotropic, nucleating fillers (A) as dispersed constituents, characterised in that the fillers (A) in layer (I), on number-weighted average of all the dispersed constituents of the fillers (A), exhibit in at least one direction (r_1) that can be chosen freely for each dispersed constituent an extension of no more than 10 nm and the individual spherulites in layer (I) exhibit in at least one plane perpendicular to the surface of the film a diameter of, on numerical average, not above 1,000 nm and not below 100 nm and the numerically predominant portion of all the dispersed constituents of the fillers (A) in layer (I) constitutes in each instance the crystal nucleus of a spherulite.

The concentration of the fillers (A) in layer (I) lies between 0.01 and 1 wt.%, relative to the overall weight of the layer (I).

The film according to the invention may contain, in addition to layer (I), one or more further polyamide-containing layers. Preferred is such a design with several layers (I) which may differ in composition and/or in grain structure.

Layer (I) and further polyamide-containing layers which are optionally present may contain conventional additives.

The fillers preferably exhibit an extension from 0.1 to 10 nm in the direction that can be chosen freely.

Preferred is a design of the film according to the invention in which the layer (I) forms an outer layer. In such a design, layer (I) preferably contains, by way of anti-blocking agents, known solid inorganic particles which protrude from the surface of the layer (I) and in this way improve the slip behaviour of the film. Suitable for this purpose are silicon oxide, calcium carbonate, magnesium silicate, aluminium silicate, calcium phosphate, talc and such like. Of these, silicon dioxide is preferably employed. Effective quantities lie in the range from 0.1 to 4 wt.%, preferably 1 to 2 wt.%. The mean particle size lies between 1 and 10 μm , preferably 2 and 7 μm , whereby particles with spherical form are particularly suitable here. Other additives that improve the surface slip of the layer (I), also in interaction with the stated solid particles that are known as anti-blocking agents, are the higher aliphatic acid amides, higher aliphatic acid esters, waxes, metallic soaps and also polydimethyl siloxanes that are conventionally designated as lubricants. The effective quantity of lubricant lies in the range from 0.01 to 3 wt.%, preferably 0.02 to 1 wt.%. Particularly suitable is the addition of higher aliphatic acid amides in the range from 0.01 to 0.25 wt.%. An aliphatic acid amide that is suitable in particular for polyamide is ethylenebisstearamide.

Layer (I) and also the further polyamide-containing layers which are optionally present contain in preferred form no further thermoplastic materials besides polyamide. The polyamide constituting, in each instance, layer (I) and also the further polyamide-containing layers which are optionally present contains in preferred form, in each instance, a mixture of various polyamides with at least 90 wt.% polyamide 6 or a copolyamide with units that are formed, in a proportion amounting to at least 90 wt.%, from ϵ -caprolactam. Besides polyamide 6, use may be made of polyamides selected from the group comprising polyamide 10, polyamide 12, polyamide 66, polyamide 610, polyamide 6I, polyamide 612, polyamide 6/66, polyamide 6I/6T, polyamide MXD6, polyamide 6/6I, polyamide 6/6T, polyamide 6/IPDI or other aliphatic or aromatic homopolyamides and

copolyamides or mixtures thereof. It proves to be particularly favourable to use no further polyamide besides polyamide 6 in layer (I) or in the further polyamide-containing layers which are optionally present.

5 Preferred is a partially crystalline grain structure of the layer (I), the crystallites of which exhibit spherulitic character in as high a proportion as possible and originate from the surface of the anisotropic particles dispersed in layer (I). Transcrystalline regions which originate and arise from the surface of the anisotropic particles dispersed in layer (I) if the polyamide containing the anisotropic, nucleating fillers is
10 cooled slowly prove to be unfavourable for the buckling resistance. In order to guarantee a buckling resistance of the film that is as high as possible, the spherulitically shaped crystallites should at the same time exhibit a diameter that is as small as possible. On the other hand, a diameter that is as large as possible is preferred for stable production of the film. A spherulite size that is preferred overall
15 is characterised by a mean size of the spherulites between 100 and 1,000 nm. By reason of the anisotropic character of the fillers, the spherulites that are formed around them may themselves be anisotropic.

The film according to the invention may contain, with a view to facilitating the heat-sealability, a single-layer or multilayer sealing layer on an outside of the multilayer
20 film. The sealing layer consequently forms the inside of the multilayer film facing towards the filling material. In preferred form the sealing layer contains the polymers or mixtures of polymers that are used conventionally as sealing medium, from the groups comprising copolymers formed from ethylene and vinyl acetate
25 (E/VA), in particularly preferred manner with a content of vinyl acetate, relative to the overall weight of the polymer, amounting to at most 20 %, copolymers formed from ethylene and unsaturated esters such as butyl acrylate or ethyl acrylate (E/BA or E/EA), copolymers formed from ethylene and unsaturated carboxylic acids (E/AA, E/MAA), in particularly preferred manner with a content of the carboxylic
30 acid comonomer, relative to the overall weight of the polymer, amounting to at most 15 %, in still further preferred form at most 8 %, salts of the copolymers formed from ethylene and unsaturated carboxylic acids, in particular E/MAA, (ionomers), in

particularly preferred manner with a content of the carboxylic acid comonomer, relative to the overall weight of the ionomer, amounting to at most 15 %, in still further preferred form at most 10 %, polyethylene of low density (PE-LD), in particularly preferred manner with a density of at least 0.91 g/cm³ and at most 0.935 g/cm³, polyethylene of high density (PE-HD), copolymers (PE-LLD) formed from ethylene and α -olefins with at least 3 C atoms, for example butene, hexene, octene, 4-methyl-1-pentene. The copolymers (PE-LLD) formed from ethylene and α -olefins can be produced with conventional catalysts or with metallocene catalysts. Of these, particularly preferred are copolymers (PE-LLD) formed from ethylene and α -olefins with a density of at least 0.90 g/cm³ and at most 0.94 g/cm³.

The multilayer film according to the invention may contain, in addition to layer (I) and also the further polyamide-containing layers which are optionally present and, optionally, in addition to the sealing layer, also one or more EVOH-containing layers for the purpose of improving the oxygen-barrier properties, whereby the EVOH-containing layers preferably contain at least 50 wt.%, relative to the overall weight of the respective EVOH-containing layer, of an EVOH with at least 85 and at most 40 mol% vinyl acetate, which is saponified to a degree amounting to at least 90 %. In a particularly preferred form an EVOH-containing layer is placed between two polyamide-containing layers.

The film according to the invention may contain one or more coupling layers in addition to layer (I) and also the further polyamide-containing layers which are optionally present, the sealing layer and/or one or more EVOH-containing layer(s). Such a coupling layer is preferably a laminating adhesive based on polyurethanes or polyester urethanes or is an extrudable coupling agent.

In addition to layer (I) and also the further polyamide-containing layers which are optionally present, the sealing layer, one or more EVOH-containing layer(s) and/or one or more coupling layer(s), the multilayer film according to the invention may contain yet further polymeric layers.

The multilayer film according to the invention can preferably be produced in flat-film extrusion lines. In this connection there is the possibility of co-extruding all or some of the layers jointly, i.e. of combining the polymers of these layers as melt streams and of causing them to flow in molten form through a common die.

Favourable is the production of the layers (I) and also of further polyamide-containing layers which are optionally present in the form of a flat film. In addition, further layers, in particular the EVOH-containing layers, can be produced in co-extrusion with layer (I) as well as further polyamide-containing layers which are optionally present.

In order to obtain the grain structure of layer (I) of the film according to the invention, after extrusion the melt containing this layer must firstly be rapidly cooled and subsequently annealed at higher temperatures.

This can be obtained in the case of the flat-film process by means of sufficiently low casting-roll temperatures, temperatures below 80°C being preferred. In this process, residence-times of at least 0.1 second should be complied with. After chilling, annealing is preferably effected on a further roll. Temperatures of at least 90°C are preferred here, temperatures of at least 100°C being particularly favourable. In this connection, residence-times of at least 0.05 second, preferably 0.1 second, are favourable. Particularly preferred, furthermore, is a chemical or mechanical modification of the surface of the constant-temperature roll in such a way that the adhesion of the film on the constant-temperature roll at high temperatures is diminished.

The temperature profile that is required for achieving the grain structure can be obtained in the case of the tubular-film process by means of a cooling in a liquid bath or in contact with surfaces moistened with liquid or in contact with flowing liquids. Use is preferably made of water as constant-temperature liquid. Favourable are temperatures of the liquid below 35°C. In this connection, residence-times of at

least 0.2 second should be complied with. After chilling, annealing is preferably effected on a further roll or in air or in a liquid bath or in contact with surfaces moistened with liquid or in contact with flowing liquids. Here temperatures of at least 60°C are preferred, temperatures of at least 85°C being particularly favourable.

5 In this connection, residence-times of at least 0.2 second are favourable.

The multilayer film according to the invention may also be subjected to a drawing operation after the extrusion. Orientation may be effected in the longitudinal direction only, in the transverse direction only, firstly in the longitudinal direction and subsequently in the transverse direction, simultaneously in the longitudinal and transverse directions, or in combinations of these steps. In this connection, drawing
10 may be carried out in respect of the entire multilayer film or in respect of partial composites thereof, in particular partial composites containing layer (I).

15 The multilayer film according to the invention may be provided on the outside or between two inner layers with a layer consisting of a metal, preferably aluminium, an oxide of a metal or of a non-metal, preferably an oxide of silicon, iron or aluminium. This layer preferably has a thickness from 5 to 200 nm. Preferred on account of the smooth surface of these layers is a coating on a layer (I), in particular
20 in such a form that the coating is not situated on the outside of the layer (I). Favourable in the case of laminated composites is a coating on the side of a layer (I) directly facing the laminating adhesive.

25 The film according to the invention may also be imprinted on the outside, on the inside or between individual layers. Preferred is an imprinting on a layer (I), in particular in such a form that the coating is not situated on the outside of the layer (I). Favourable in the case of laminated composites is a coating on the side of a layer (I) directly facing the laminating adhesive.

30 Surprisingly it was found that the film according to the invention attains, besides the outstanding optical appearance, a very high degree of stiffness with good surface slip.

The film according to the invention exhibits in addition very good flatness and high dimensional stability. In addition to a good winding capability, it can therefore be subjected - in-line or in separate operations - to a further processing step such as lamination, coating or imprinting.

By virtue of the unexpectedly high rates of production that can be attained, an optimal utilisation of operational resources is possible.

Surprising furthermore was the fact that the use of small quantities of a nanodisperse, anisotropic, nucleating filler already makes the good technical-production properties possible. Neither in the case of conventional anisotropic filler systems such as glass fibres or mica nor in the case of the nanoscalar fillers that are used do appropriate dosages result in a significant increase in the stiffness of polyamides containing them. Higher dosages of the nanodisperse fillers, on the other hand, bring about an embrittlement of the film. In addition, in the flat-film process they generate a corrugation of the film on the casting roll and consequently do not permit any qualitatively utilisable production.

The film according to the invention turns out to be imprintable in surprisingly brilliant manner and well capable of having barrier layers vapour-deposited.

With the general properties obtained in a composite with a sealing layer, the film according to the invention is suitable for packaging purposes in particular. In addition, the film according to the invention turns out to be surprisingly well thermoformable.

The invention therefore further provides the use of the film for the production of packaging material, in particular for the production of thermoformed food containers.

Examples

On the basis of the Examples according to the invention and the Comparative Examples, the following properties were determined as follows:

5

- The modulus of elasticity according to DIN EN ISO 527 at a temperature of 23°C and with a relative moisture of 50 %. In this connection the specimen was taken from a film roller and conditioned for 48 hours prior to the measurement in the measuring climate.

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- The haze according to ASTM D 1003.
- The gloss on the outside of the film at an angle of 20° according to DIN 67530.

15

- The frictional behaviour according to DIN 53 375. The coefficients of friction are measured in respect of the sliding friction between film and film. The measurement was carried out at 23°C.

20

- Investigation by transmission electron microscopy of a cross-section of the film. To this end, a thin section was taken from the PA outer layer of the film in the transverse direction and was contrasted with formaldehyde solution and OsO₄. The grain structure was characterised on the basis of a print-out with a magnification of 15,000:1 as follows:

25

- is a substantially spherulitic crystal structure present?
- does the numerically predominant portion of all the dispersed constituents of the fillers in the PA outer layer constitute the crystal nucleus of a spherulite?
- mean number-weighted size of the spherulites in the case where a substantially spherulitic grain structure is present.

30

- The producibility as flat film under the stated conditions. In particular, the stability and flatness of the film were evaluated. In this connection, stability means the capability of the film to be guided through the line without sticking and without overstretching and in particular to be capable of being wound. Flatness means the absence of wrinkles and local instances of overstretching which, as a rule, arise as described above in the course of leaving the casting roll and which are impressed on the constant-temperature roll. In addition, the observation was made that highly filled films form an undesirable corrugated structure on the casting roll. The appearance of such a structure resulted in a negative appraisal. The results were classified - where appropriate differentiated according to flatness, stability and formation of corrugations - in the categories ++ (very good), + (good), - (poor).
 - ++ without detectable after-shrinkage, cylindrical roller
 - + slight after-shrinkage detectable
 - distinct after-shrinkage detectable
 - strong after-shrinkage detectable
- After-shrinkage on the roller after storage for two weeks at 15 to 20°C and with 40 to 70 % relative moisture. A visual appraisal was made according to deviations from the cylindricity of the roller towards an irregular surface as follows:

Test Series 1:

- Single-layer flat films consisting of polyamide 6 with a thickness of 30 µm were manufactured on a flat-film extrusion line of conventional design. The casting roll has a peripheral speed of 100 m/min. The residence-time of the film on the casting roll amounted to 0.5 second. The residence-time on the constant-temperature roll directly following the casting roll amounted to 0.2 second. The width of the films amounted to 1,200 mm. The polyamide 6 that was used contains 600 ppm ethylenebisstearamide and approximately 150 ppm talc by way of nucleating agent. It exhibits a relative solution viscosity of 3.8 in m-cresol. The temperatures of the

rolls were varied within the test series. The optical properties, the stiffness, the after-shrinkage and also the producibility were evaluated. None of the settings is suitable for the object as stated.

- 5 In Comparative Example 1.1 (V1.1) the temperature of the casting roll amounted to 120°C and the temperature of the constant-temperature roll amounted to 80°C.
In Comparative Example 1.2 (V1.2) the temperature of the casting roll amounted to 40°C and the temperature of the constant-temperature roll amounted to 40°C.
In Comparative Example 1.3 (V1.3) the temperature of the casting roll amounted to
10 70°C and the temperature of the constant-temperature roll amounted to 120°C.

The results for Test Series 1 are summarised in the table below:

Feature (unit)	Example (B) or Comparative Example (V)		
	PA6, 30 µm		
	V1.1	V1.2	V1.3
Temperature of casting roll (°C) / temperature of cooling roll (°C)	120 / 80	40/ 40	70 / 120
Spherulitic grain structure?	yes	yes	yes
Mean spherulite size (nm)	about 1500	about 10	about 300
Gloss (gloss units)	121	155	166
Haze (%)	7.4	0.6	1.7
Modulus (MPa)	1740	801	1216
Coefficient of sliding friction film against film (-)	0.32	2.2	0.67
After-shrinkage (%)	++	--	+
Producibility (flatness)	++	-	-
Producibility (stability)	++	-	+

- 15 Depending on the temperature control of the rolls, the film consisting of unfilled PA6 is either unsatisfactory as regards the optical properties or exhibits inadequacies

as regards producibility and surface slip. In this connection, advantages arise in the case of a cold casting roll with respect to the stability of the web as a result of after-annealing. The problems with the flatness, however, cannot be eliminated.

5 **Test Series 2:**

Flat films were manufactured under the conditions of Comparative Example 1.3. By way of polyamide, use was made of polyamide 6, filled with 2 wt.% of an inorganic, anisotropic filler.

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By way of filler in Comparative Example 2.1, use was made of platelet-like mica with a mean particle diameter of 25 μm and a mean thickness of 0.5 μm . The mica was dispersed in the polyamide in a twin-screw extruder, the extrudate was subsequently granulated, blended with unfilled polyamide 6 and processed into a flat film as in Comparative Example 1.3.

15

In Comparative Example 2.2, use was made of a polyamide 6 with a relative solution viscosity of 3.6 in m-cresol, containing 2 % by weight of nanoscalar phyllosilicate (montmorillonite) dispersed in platelet-like form. The montmorillonite particles exhibit thicknesses of approximately 1 nm and diameters from 100 to 1,000 nm.

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Once again, only the optical properties, the after-shrinkage and also the producibility were evaluated. As in Test Series 1, it turned out that none of the settings was suitable for the object as stated.

25

The results for Test Series 2 are summarised in the table below:

Feature (unit)	Example (B) or Comparative Example (V)	
	PA6, 30 μ m, casting roll = 70°C, cooling roll = 120°C	
	V2.1	V2.2
Filler	2 % mica	2 % montmorillonite
Spherulitic grain structure?	yes	yes
Are fillers predominantly crystal nuclei ?	no	yes
Mean spherulite size (nm)	about 300	about 300
Gloss (gloss units)	99	not measurable, since corrugated
Haze (%)	8.3	2.1
Modulus (MPa)	1319	2159
Coefficient of sliding friction film against film (-)	0.29	0.43
After-shrinkage (%)	+	not measurable, since corrugated
Producibility (flatness)	-	-- (corrugated)
Producibility (stability)	+	++

5 Mica accordingly shows no properties improving the flatness, but the film fogs strongly and loses gloss. However, the surface slip is improved. The film containing 2 % montmorillonite cannot be processed on the casting roll and completely characterised, by reason of strong formation of corrugations. However, the stiffness is noticeably increased. All in all it proves to be unusable.

Test Series 3:

10

For comparison, the materials from Test Series 2 were processed into films under the conditions as in Comparative Example 1.2, i.e. without after-annealing. The same properties as in Test Series 2 were investigated.

The results for Test Series 3 are summarised in the table below:

Feature (unit)	Example (B) or Comparative Example (V) PA6, 30 μ m, casting roll = 40°C, cooling roll = 40°C	
	V3.1	V3.2
Filler	2 % mica	2 % montmorillonite
Spherulitic grain structure?	yes	yes
Are fillers predominantly crystal nuclei ?	no	no
Mean spherulite size (nm)	about 10	about 10
Gloss (gloss units)	104	not measurable, since corrugated
Haze (%)	7.9	2.0
Modulus (MPa)	813	1498
Coefficient of sliding friction film against film (-)	1.03	1.42
After-shrinkage (%)	--	not measurable, since corrugated
Producibility (flatness)	-	-- (corrugated)
Producibility (stability)	-	+

- 5 Also in the case of a mode of production without after-annealing, the addition of mica yields no advantages with respect to stiffness and producibility in comparison with unfilled polyamide 6. Disadvantages merely arise in optical respects. The film containing 2 % montmorillonite cannot be processed on the casting roll and completely characterised, once again by reason of strong formation of corrugations.
- 10 Hence it proves to be unusable, despite the high degree of stiffness and good transparency. The stability of the web is lower compared to Comparative Example 2.2 with after-annealing but is still acceptable.

Test Series 4:

Under the conditions as in Comparative Example 1.2, i.e. with cold casting roll and constant-temperature roll, an attempt was made to eliminate the problem of the formation of corrugations through a reduction in the content of montmorillonite. To this end, the polyamide 6 containing 2 % montmorillonite from Comparative Example 2.2 was blended with the unfilled polyamide 6 from Comparative Example 1.1 in such a way that proportions of the montmorillonite in the mixture arise amounting to 0.2 and 1.0 wt.%. The characterisation of the film yielded the result listed in the following table:

Feature (unit)	Example (B) or Comparative Example (V) PA6, 30 µm, casting roll = 40°C, cooling roll = 40°C	
	V4.1	V3.2
Filler	0.2 % montmorillonite	1.0 % montmorillonite
Spherulitic grain structure?	yes	yes
Are fillers predominantly crystal nuclei ?	no	no
Mean spherulite size (nm)	about 10	about 10
Gloss (gloss units)	163	157
Haze (%)	1.2	1.8
Modulus (MPa)	926	1175
Coefficient of sliding friction film against film (-)	2.02	1.95
After-shrinkage (%)	-	-
Producibility (flatness)	-	-
Producibility (stability)	-	-

Although the films that were manufactured using a mode of production without after-annealing with lowered content of montmorillonite show no formation of corrugations on the casting roll, the stability of the film and also the stiffness and flatness thereof decrease. The films are not capable of sliding well. In addition,

after-shrinkage occurs on the reel. Consequently, corresponding films are likewise not suitable for the object as stated.

Test Series 5:

5 Films with graduated content of montmorillonite were manufactured under the conditions as in Comparative Example 1.3, i.e. with cold casting roll and subsequent after-annealing on the constant-temperature roll. To this end, the content of montmorillonite was varied in the same way as in Test Series 4. Proportions of 0.05
10 wt.%, 0.2 wt.%, and 1 wt.% were set. In addition, 1,000 ppm of a kaolin with a particle size of about 2 μm were added by way of anti-blocking agent. For comparison, the Comparative Examples 1.3 and 2.2 with 0 wt.% and 2.0 wt.% respectively, but without anti-block, are also listed. The characterisation of the films yielded the result listed in the following table:

Feature (unit)	Example (B) or Comparative Example (V) PA6, 30 μ m, filled with montmorillonite casting roll = 70°C, cooling roll = 120°C				
	V1.3	B5.1	B5.2	B5.3	V2.2
Proportion by weight of montmorillonite	0 %	0.05 %	0.2 %	1.0 %	2.0 %
Spherulitic grain structure?	yes	yes	yes	yes	yes
Are fillers predominantly crystal nuclei ?	yes	yes	yes	yes	yes
Mean spherulite size (nm)	about 300	about 300	about 300	about 300	about 300
Gloss (gloss units)	166	157	162	168	*
Haze (%)	1.7	1.8	1.6	2.0	2.1
Modulus (MPa)	1216	1456	1650	1803	2159
Coefficient of sliding friction film against film (-)	0.67	0.42	0.45	0.39	*
After-shrinkage (%)	+	++	++	++	++
Producibility (flatness)	-	+	++	++	-- (corrugated)
Producibility (stability)	+	++	++	++	++

* not measurable on account of corrugations

5. Examples 5.1 to 5.3 according to the invention turn out to be appropriate, in all respects, for the object as stated.

Claims

1. A film with at least one layer (I) consisting of substantially spherulitically crystallised polyamide containing solid, anisotropic, nucleating fillers (A) as dispersed constituents, characterised in that the fillers (A) in layer (I), on number-weighted average of all the dispersed constituents of the fillers (A), exhibit in at least one direction (r1) that can be chosen freely for each dispersed constituent an extension of no more than 10 nm and the individual spherulites in layer (I) exhibit in at least one plane perpendicular to the surface of the film a diameter of, on numerical average, not above 1,000 nm and not below 100 nm and the numerically predominant portion of all the dispersed constituents of the fillers (A) in layer (I) constitutes in each instance the crystal nucleus of a spherulite.
2. Film according to claim 1, characterised in that it contains one or more further polyamide-containing layers.
3. Film according to claim 1, characterised in that one or more layers (I) and/or one or more further polyamide-containing layers contain polyamide which is formed in a proportion amounting to at least 90 percent by weight from ϵ -caprolactam.
4. Film according to one of the previous claims, characterised in that the individual spherulites are anisotropic in at least one layer (I).
5. Film according to one of the previous claims, characterised in that the layer (I) forms the outer layer of the film.
6. Film according to one of the previous claims, characterised in that it contains one or more further polymeric layer(s) or contains between two layers a layer consisting of a metal or metal oxide or contains an imprint.

7. A process for producing a film with at least one layer (I) from substantially spherulitically crystallised polyamide containing solid anisotropic nucleating fillers as flat film by
- 5
- (1) melting down the polymers and forming the polymer melt into shape via a flat-film extrusion die
- (2) cooling of the polymer melt and solidification into a solid film on a rotating roll which has a temperature of at most 80°C, for at least 0.1
- 10 second
- (3) heating of the film on a rotating roll which has a temperature of at least 90°C, for at least 0.05 second.
8. Use of a film according to one of the previous claims 1 to 6 for the
- 15 production of containers on shaping/filling/sealing machines.
9. Use of a film according to one of the previous claims 1 to 6 for the packaging of foodstuffs.

**COMBINED DECLARATION AND POWER OF ATTORNEY**

ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought

on the invention entitled

FLEXIBLE FILM PROVIDED WITH A FINE SPHERULITIC POLYAMIDE LAYER CONTAINING NANOSCALAR, ANISOTROPIC NUCLEATING AGENTS

the specification of which is attached hereto,

or was filed on **October 14, 1999**

as a PCT Application Serial No. **PCT/EP99/07716**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

198 47 844.5 (Number)	Germany (Country)	October 16, 1998 (Month/Day/Year Filed)
198 47 845.3 (Number)	Germany (Country)	October 16, 1998 (Month/Day/Year Filed)
199 35 324.7 (Number)	Germany (Country)	July 28, 1999 (Month/Day/Year Filed)
199 37 117.2 (Number)	Germany (Country)	August 6, 1999 (Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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FULL NAME OF SECOND INVENTOR <u>Andreas Gasse</u>		INVENTOR'S SIGNATURE <i>Andreas Gasse</i>	DATE <u>1.3.2001</u>
RESIDENCE D 29664 Walsrode, Germany DEX		CITIZENSHIP German	
POST OFFICE ADDRESS Ricarda-Huch-Strasse 17, D 29664 Walsrode, Germany			
FULL NAME OF THIRD INVENTOR <u>Bernd Eilers</u>		INVENTOR'S SIGNATURE <i>Bernd Eilers</i>	DATE <u>9.3.01</u>
RESIDENCE D 29699 Bomlitz, Germany DEX		CITIZENSHIP German	
POST OFFICE ADDRESS Berthold-Schwarz-Strasse 1, D 29699 Bomlitz, Germany			
FULL NAME OF FOURTH INVENTOR <u>Rudi Klein</u>		INVENTOR'S SIGNATURE <i>Rudi Klein</i>	DATE <u>23.3.01</u>
RESIDENCE D 29664 Walsrode, Germany DEX		CITIZENSHIP German	
POST OFFICE ADDRESS Krelingen 86a, D 29664 Walsrode, Germany			
FULL NAME OF FIFTH INVENTOR <u>Claudia Müller</u>		INVENTOR'S SIGNATURE <i>Claudia Müller</i>	DATE <u>23.03.2001</u>
RESIDENCE D 29664 Walsrode, Germany DEX		CITIZENSHIP German	
POST OFFICE ADDRESS Hermann-Löns-Strasse 6, D 29664 Walsrode, Germany			
FULL NAME OF SIXTH INVENTOR <u>Gregor Kaschel</u>		INVENTOR'S SIGNATURE <i>Gregor Kaschel</i>	DATE <u>26.3.2001</u>
RESIDENCE D 29699 Bomlitz, Germany DEX		CITIZENSHIP German	
POST OFFICE ADDRESS Uferstrasse 37, D 29699 Bomlitz, Germany			
FULL NAME OF SEVENTH INVENTOR <u>Rainer Brandt</u>		INVENTOR'S SIGNATURE <i>Rainer Brandt</i>	DATE <u>23.3.2001</u>
RESIDENCE D 29664 Walsrode, Germany DEX		CITIZENSHIP German	
POST OFFICE ADDRESS Am Berge 8, D 29664 Walsrode, Germany			

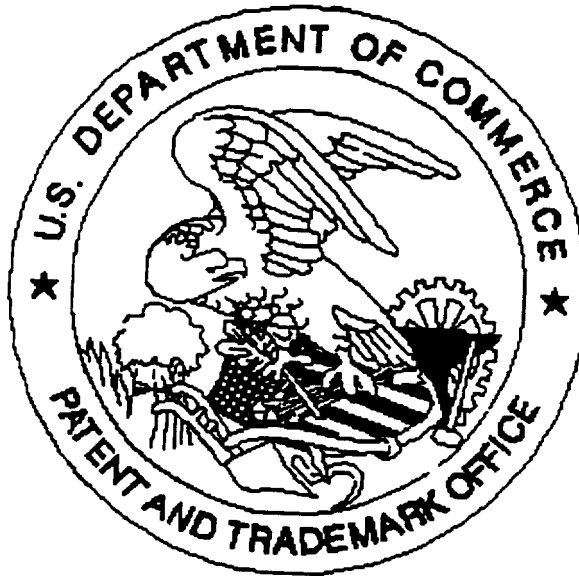
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FULL NAME OF EIGHTH INVENTOR <u>Dieter Neubauer</u>		INVENTOR'S SIGNATURE <i>Dieter Neubauer</i>	DATE <u>26.03.01</u>
RESIDENCE D 29699 Bomlitz, Germany		CITIZENSHIP German	
POST OFFICE ADDRESS Am Eichenkamp 37, D 29699 Bomlitz, Germany			
FULL NAME OF NINTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF TENTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF ELEVENTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF TWELFTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF THIRTEENTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF FOURTEENTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF FIFTEENTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF SIXTEENTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF SEVENTEENTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
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